

PHOTOPHORESIS AND PROPERTIES
OF SOOT
IN TWO PARTS

UCID- 20534

PHOTOPHORESIS AND PROPERTIES OF SOOT

A. A. Broyles
J. R. Ipser

September 1985

Lawrence
Livermore
National
Laboratory

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$, Microfiche \$4.50

<u>Page Range</u>	<u>Domestic Price</u>	<u>Page Range</u>	<u>Domestic Price</u>
001-025	\$ 7.00	326-350	\$ 26.50
026-050	8.50	351-375	28.00
051-075	10.00	376-400	29.50
076-100	11.50	401-426	31.00
101-125	13.00	427-450	32.50
126-150	14.50	451-475	34.00
151-175	16.00	476-500	35.50
176-200	17.50	501-525	37.00
201-225	19.00	526-550	38.50
226-250	20.50	551-575	40.00
251-275	22.00	576-600	41.50
276-300	23.50	601-up ¹	
301-325	25.00		

¹Add 1.50 for each additional 25 page increment, or portion thereof from 601 pages up.

PHOTOPHORESIS AND PROPERTIES OF SOOT

A. A. Broyles and J. R. Ipser

Lawrence Livermore National Laboratory, University of California

Livermore, CA 94550 U.S.A.

I. INTRODUCTION

An essential element in the calculations of the global effects of a nuclear winter is the altitude of deposition of smoke produced in the fires. Smoke is removed primarily by rain in the lower part of the troposphere. Smoke at higher altitudes must be brought downward by air currents unless some force such as gravity or photophoresis from sunlight can have an important influence. We shall consider this last possibility here.

Calculations by Penner, Haselman, and Edwards (1985) indicate that, although smoke from firestorms may reach the stratosphere, initially it descends again until it is at or below the tropopause. Less intense fires deposit smoke at lower levels of the troposphere. For this reason, we shall be primarily concerned with the effect of photophoresis on particles in the troposphere that we shall take to range from 1 to 10 kilometers. A word of caution should be written on this point, however, since it has been pointed out that the sun's light may heat the smokey air and cause it to rise into the stratosphere.

According to Penner and Haselman (1985), the number density curve for smoke particles as a function of size has its maximum at a radius between 0.1 and 1.0 microns. In addition, since the wavelength of maximum intensity in sunlight is around 0.55 microns, particles with radii between 0.1 and 1.0 microns have the highest efficiency for scattering and absorbing. We will be most interested in particles of these sizes.

It is true that some dust from the earth's surface will be lofted into the stratosphere by explosions greater than 30 kilotons, but the fraction of the bomb fragments injected into the stratosphere does not reach 50% until the bomb energy yield exceeds 350 kilotons. Dust is much less effective relative to smoke in absorbing light. Nevertheless, with the nuclear arsenals currently in existence, enough dust can reach the stratosphere to reduce the sunlight by a serious amount in an all-out war. Fortunately, the increasing accuracy of missile guidance system makes it wasteful to use large-yield weapons so that the amount of dust to be expected in the stratosphere is likely to decrease with improvements in the weapons arsenals.

According to Tangren, McMahon, and Ryan (1976), particulate matter in forest fire smoke consists of both solid matter and liquid hydrocarbons. The component that most effectively absorbs light is carbon in the form of soot. We shall concentrate largely on the photophoretic forces on soot.

II. THE AVAILABLE LITERATURE

At least three kinds of photophoretic forces have been proposed that may act on particles in the atmosphere. The ranges of validity of these theories for spheres are defined in terms of the Knudson number, that is, the mean free path of the air molecules divided by the radius of the particle. Two of them can be applied to spheres with Knudson numbers larger than unity while the third describes forces on those with Knudson numbers smaller than unity (the hydrodynamic region). Unfortunately the comparison of these theories with experiment has not been very satisfactory, often giving agreement only to a little less than an order of magnitude. In addition, there is some doubt as to the validity of these theories when the Knudsen numbers are in the vicinity of unity. Again unfortunately, as we shall see, the range of Knudsen numbers that interests us for calculating the photophoretic forces for particles includes unity. Since there is reason to believe that the equations that are derived for particles with small Knudsen numbers (hydrodynamic region) may hold for

numbers larger than expected (Alder, Alley, and Pollock, 1981), and since a large part of the range of interest for us has small Knudsen numbers, we shall use these equations for all of the particles in the air from 0 to 10 kilometers.

Rohatschek (1985) has compared the two theories for large Knudsen numbers with his experiments. One of them considers a force that results when a particle is unevenly heated. Molecules leave the warmer portion of the surface with a higher momentum than those from the colder surface giving larger impulses to the hotter side of the particle. Detailed calculations for this kind of force are presented by Sitarski and Kerker (1984). Rohatschek finds, however, that a much larger force can be explained by noting that a particle that is hotter than the surrounding air will more effectively transmit energy to the molecules on a rough portion of its surface than on a smooth part. This is because the air molecules may bounce around in the crevices of the rough surface and gain more energy. The result is that the particle will be propelled away from its rough side.

Equations for the photophoretic forces on spherical particles have been derived by Yalamov, Kutukov, and Shchukin (1976) using hydrodynamic and heat conduction equations. The solutions are very complicated, but a limiting form has been used by Pluchino (1983) to calculate the force on particles with small Knudsen numbers. This form is

$$F = -4\pi r \mu^2 K I J / D_a T k. \quad (1)$$

where K is an empirically adjusted constant that we take to be 1.275, r and k are the particle radius and thermal conductivity. μ , D_a , and T are the viscosity, density, and temperature of the air, I is the solar radiation intensity (1350 watts per square meter), and

$$J = (3/2) n m x \int_0^1 r^3 dr \int_0^\pi \sin 2\theta (E/E_o)^2 d\theta, \quad (2)$$

Here,

$$x = 2\pi r / w. \quad (3)$$

where w is the wave length of the incident light beam, n and m are the real and imaginary parts of the particle's index of refraction, and E and E_o are the local and incident electric field magnitudes.

The quantity J gives the distribution of heat deposited by the radiation incident on the particle. This distribution has been calculated for several particle sizes and indices of refraction by Dusel, Kerker, and Cooke (1979) and by Pluchino (1983).

In subsequent sections we will consider the input data for the above equations. It is useful to indicate the importance of the photophoretic force given by Eq. (1) by computing the terminal velocity that it imparts to particles of various sizes when they are at various altitudes. We will first compute the terminal velocities for particles under the influence of gravity alone and then determine the ratio of the photophoretic force F to that due to gravity G . Multiplying the terminal velocity due to gravity by F/G gives the terminal velocity produced by photophoresis.

III. PROPERTIES OF AIR AND THE RANGE OF KNUDSEN NUMBERS

The mean free path of gas molecules is equal to the reciprocal of the product of the cross section and the particle number density. The average cross section will have only a slight dependence on temperature so that the variation of mean free path with altitude will be essentially that of the reciprocal of the density of air D_a . The altitude dependence of density is approximately given by (Broyles 1985)

$$D_a = 1.2e^{-0.104h} kg/m^3 \quad (4)$$

where h is the altitude in kilometers.

Since the mean free path at sea level is 0.066 microns (Pruppacher and Klett 1980), as a function of altitude, it is

$$m.f.p. = 0.066e^{0.104h} \text{ microns.} \quad (5)$$

We can divide the mean free paths given by this formula by the particle radii to obtain the Knudsen numbers listed in Table 1. As we have previously noted, these numbers bracket unity although in the troposphere more of them are less than one.

TABLE 1. Knudsen numbers, gravitational terminal velocities V , slip factors S , and photophoretic terminal velocities V_p for particles in the atmosphere.

Radius (μ)	0.1	0.1	0.1	1.0	1.0	1.0
Altitude (km)	0	10	20	0	10	20
Knudsen number	0.7	1.9	5.3	0.07	0.2	0.5
$V \times 10^4$ km/week	2.1	5.3	16	1.8	2.5	4.4
Slip factor (S)	1.9	3.8	9.4	1.1	1.2	1.7
$V_p \times 10^4$ km/week	4.0	8.5		-0.31	-0.42	

An equation for the viscosity of air can be found on page 283 of the Smithsonian Meteorological Tables (1963). It is equivalent to

$$\mu = \mu_o (T/288)^{\frac{1}{2}} / [1 - .294(1 - 288/T)], \quad (6)$$

where

$$\mu_o = 1.8 \times 10^{-5} \text{ kg/sm.} \quad (7)$$

Since, for an ideal gas, the temperature is proportional to the pressure divided by the density, we can use Eqs. (48) and (49) from Broyles (1985) to arrive at

$$T = 288e^{-.026h} \text{ } ^\circ K \quad (8)$$

where, again, h is the altitude in kilometers. The last two equations can be used to determine μ at any altitude.

IV. PROPERTIES OF SOOT

Recent experiments on soot produced in an acetylene flame have led George Mulholland (private communication) to an empirical formula for the density of soot particles as a function of radius. Since soot is made up of chains of carbon particles whose radii are of the order of 0.015 microns, we shall adjust this formula to reach the density of solid carbon as the radius approaches 0.015. This gives a soot particle density of

$$D = 2.3 / [R(1 - 0.0042/R)]^{1.8} \text{ kg/m}^3 \quad (9)$$

where R is the radius of giration $(\sum_i m_i r_i^2 / M)$ measured in microns. For soot particles with radii ranging from 0.1 to 1.0 microns, the last term in the parentheses is negligible which reduces the formula to the one originally obtained by Mulholland.

In order to calculate F with the aid of Eq. (1), we need the thermal conductivity k for soot. Unfortunately, this number is not available in the literature. Since soot is made up of carbon and air, its thermal conductivity must lie somewhere between the conductivities for these two materials. Graphite is listed in the Handbook of Chemistry and Physics as having a conductivity 125 watts/ $m^\circ K$ perpendicular to the planes and 80 watts/ $m^\circ K$ parallel to the planes. This indicates the large variation in this quantity.

Rohatschek (1985) has measured thermal conductivities and found that graphite, copper, and aluminum show a variation of it with the fourth power of density. Figure 1 plots the thermal conductivity against density for several forms of carbon-air mixtures and several kinds of wood. The points plotted (from values listed in the American Institute of Physics Handbook, 1972) fall within a factor of two of a single curve covering four orders of magnitude. A rough fit to this curve is given by

$$k = 1.5 \times 10^{-13} D^{4.5} + .00015 D + .024 \text{ W/m}^\circ K. \quad (10)$$

The first term on the left varies as the 4.5 power rather than Rohatschek's fourth power. The constant term is the value of k for air under normal conditions.

Finally, in order to compute the energy deposition J in Eq. (2), the index of refraction must be known. We may think of a soot particle as a polarizable medium with the primary contribution coming from the carbon. To compute the index of refraction of these particles, it is convenient to use the Clausius-Mossotti equation (Jackson, 1975, p. 155). This equation is equivalent to

$$(\epsilon_s - 1)/(\epsilon_s + 2) = (D_s/D_c)(\epsilon_c - 1)(\epsilon_c + 2) \quad (11)$$

where ϵ is the dielectric constant and the subscript c indicates solid carbon while s indicates the soot particle. Pluchino, Goldberg, Dowling, and Randall (1980) have measured the index of refraction of small carbon balls and found that

$$n_c - i m_c = (1.7 \pm 0.12) - i (0.8 \pm 0.09). \quad (12)$$

Since

$$\epsilon = (n - i m)^2, \quad (13)$$

we can compute ϵ_c and substitute it into Eq. (11). The density of graphite is 2240 kg/m^3 and for soot is given by Mulholland's formula, Eq. (9). When we substitute D_c into Eq. (11), we can expand in powers of D_c to find ϵ_s and then take the square root to obtain

$$\begin{aligned} n_s - i m_s = & 1 + 3.4 \times 10^{-4} D_s + 7.2 \times 10^{-8} D_s^2 \\ & - i \left(2.2 \times 10^{-4} D_s + 2.4 \times 10^{-8} D_s^2 \right) + . \end{aligned} \quad (14)$$

With this formula and Eq. (6), we can compute the numbers in Table 2. These can be compared with the index of refraction for air which is 1.0002926.

V. TERMINAL VELOCITY UNDER GRAVITY

The solutions to the equations solved by Yalamov, Kutukov, and Schukin (1976) have a limiting form that consists of the force given in Eq. (1) balanced by the drag force given by Stokes law. These forces balance at the terminal velocity. As we have already noted,

TABLE 2. Densities and indices of refraction for soot as a function of radius.

R(microns)	0.1	0.2	1.0
$D_s(\text{kg./m}^3)$	157	43	2.32
n_s	1.055	1.014	1.00079
m_s	0.035	9.5×10^{-4}	5.1×10^{-4}
J	2.1×10^{-4}	-1.3×10^{-4}	-2.2×10^{-5}
F/G	1.6	-0.98	-0.17

we will compute the terminal velocity under the force of gravity first and then multiply it by the ratio F/G.

The force due to gravity is

$$G = (4\pi/3)r^3 Dg, \quad (15)$$

where g is the acceleration due to gravity. When this is equated to the magnitude of the drag force given by Stokes' law,

$$\text{Drag} = 6\pi r\mu V/S, \quad (16)$$

the resulting equation can be solved for

$$V = 2r^2 SgD/(9\mu), \quad (17)$$

where S is called the "slip factor" and accounts for the deviation from hydrodynamic motion of the air because of a large mean free path. It is

$$S = 1 + y(1.257 + 0.4e^{-1.1y}), \quad (18)$$

where

$$y = m.f.p./r. \quad (19)$$

Values of V for soot are listed in Table 1. The deviation of S from unity is a measure of the uncertainty of the validity of Stokes' law and so it is also listed in Table 1.

It is clear from the table that soot particles in the troposphere in the size range of 0.1 to 1.0 microns have terminal velocities of the order of 10^{-4} kilometers per week. Thus, unless F/G exceeds 10^3 , the photophoretic force on a soot particle will be negligible.

VI. CALCULATING THE ENERGY DISTRIBUTION

Ipser (1985) has derived an approximate expression for J for a sphere in Eq. (2) using geometrical optics. In his analysis, the side of the particle that is most heated is determined by competition between the rate of absorption of radiation (determined by the imaginary part of the index of refraction) and the focusing (determined largely by the real part). The absorption tends to heat the particle on the upper side (toward the sun) while the focusing concentrates the light on the back side.

Ipser can calculate the average heating in the hemisphere toward the light and in the hemisphere away from the light. The difference gives an estimate for J . The ratio f of the focal length of a sphere to the radius is related to the index of refraction by

$$f = [2(n - 1)]^{-1}. \quad (20)$$

Ipser's formula for $f \gg 1$ and $xm \ll 1$ in terms of expansions in $1/f$ and xm is

$$J = \langle \hat{T} \rangle + \langle 2(r/r) \cos \theta \rangle + (3mx/8f) \left[(1 - 8/15f) - 2mx f (1 + 16/15f + 1/3f^2 + \dots) \right], \quad (21)$$

where x is defined in Eq. (3), and m is the negative imaginary part of the index of refraction of the particle. The quantity \hat{T} is the fraction of light transmitted per unit volume.

An upper limit for J results from replacing the two averaged quantities by unity. The values of J in Table 2 have been calculated from these formulas using the parameters listed in that table. A minimum in J occurs near a particle radius of 0.2 microns. It is interesting to note that the values of J calculated by Pluchino (1982) have magnitudes of the order of or less than 0.1. He used the indices of refraction for glycerol at wave lengths of 10.63 microns.

VII. CALCULATING F/G

We can now divide Eq. (1) by Eq. (15), to get an equation for F/G. If, in addition we substitute the intensity of sunlight, 1350 W/m^2 , for I , we have

$$F/G = 5.27 \times 10^{14} \mu^2 J / (D_a D T k R^2). \quad (22)$$

Since the variation of the properties of air in the troposphere is very small, we can substitute the values for zero altitude. Then the last equation reduces to

$$F/G = 494 J / (k R^2 D). \quad (23)$$

Furthermore, the values of $k R^2 D$ for soot particles differ from 0.06 by less than 20%. This is not surprising since D in Eq. (9) varies approximately as R^{-2} . Substituting this value into the last equation then gives

$$F/G = 8200 J, \text{ soot in the troposphere.} \quad (24)$$

We can now substitute the upper limits for the values of J listed in Table 2 to obtain the upper limits on F/G shown there. These, in turn, can be multiplied by the values of the terminal velocity appearing in Table I to give the terminal velocities V_p for the photophoretic forces shown there. It is clear that these terminal velocities are far too small to be of significance in the calculation of the motion of soot in the atmosphere.

VIII. DISCUSSION

The model of a soot particle used here assumes that air flows around it as though it were a solid sphere. Of course the open structure must allow some flow of air through it. In addition, the indexes of refraction listed in Table 2 are so near to unity that the amplitudes of the incident waves on each component of the soot agglomerate must not differ by much. This suggests that the forces on each elemental carbon particle may be relatively independent of the presence of the others. Thus it would be reasonable to make

a calculation using a model assuming that each of these elemental carbon particles acts independently.

The use of an index of refraction and the Clausius-Mossotti can be expected to be advisable when the wavelength of light is large compared to the spacing between the elementary carbon particles in the soot agglomerate. The spacing of these elements in a typical soot particle seems to be of the order of the visible light wavelength of 0.55 microns used here. For infrared light, however, the use of an index of refraction is well justified. Assuming the scattering of the elementary carbon particles to be independent is a possible alternative, but it would neglect the effects of absorption, diffraction, and focusing by the agglomerate as a whole. Nevertheless, it would be useful to calculate F in this manner for comparison. It seems unlikely, however, that such a calculation would alter the conclusion that the photophoretic forces can be ignored in determining the motion of soot particles in the troposphere.

As we have noted, however, the forces on soot particles at the low pressures high in the stratosphere may be quite different from those obtained here and must be calculated by entirely different formulas.

ACKNOWLEDGMENTS

George Mulholland kindly reviewed the manuscript for this paper and made most constructive comments. Others who made very useful suggestions include Leonard Rosen, William Porch, Joyce Penner and Charles Shapiro. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

REFERENCES

- Alder, B. J., W. E. Alley, and E. L. Pollock (1981). Ber Bunsenges. *Phys. Chem.*, **85**, 944.
- American Institute of Physics (1972). *American Institute of Physics Handbook, 3rd Edition* (McGraw-Hill, New York).
- Broyles, A. A. (1985). *Am. J. Phys.*, **53**, 323.
- Ipsier, James R. (1985). Lawrence Livermore National Laboratory Report UCID-20541, Livermore, CA 94550.
- Jackson, J. D. (1975). *Classical Electrodynamics*, second edition (John Wiley, New York).
- Penner, J. E. and L. C. Haselman, Jr. (1985). Lawrence Livermore National Laboratory Report UCRL-92523, Livermore, CA 94550.
- Penner, J. E., L. C. Haselman, Jr., and L. L. Edwards (1985). Lawrence Livermore National Laboratory Report UCRL-90915, Livermore, CA 94550.
- Pluchino, A. B. (1983). *Appl. Opt.*, **22**, 103.
- Pluchino, A. B., S. S. Goldberg, J. M. Dowling, and C. M. Randall (1980). *Appl. Opt.*, **19**, 3370.
- Pruppacher, H. R. and J. D. Klett (1980). *Microphysics of Clouds and Precipitation*, (D. Reidel, Boston).
- Rohatschek, Hans (1985). *J. Aerosol Sci.*, **16**, 29.
- List, R. J. (1963). *Smithsonian Meteorological Tables*. Smithsonian Institute, Washington.
- Tangren, C. D., C. K. McMahon, and P. W. Ryan (1976). *Contents and Effects of Forest Fire Smoke*, Southern Forest Fire Laboratory, Southeastern Forest Experiment Station, USDA Forest Service, Macon, Georgia.
- Yalamov, Y. I., V. B. Kutukov, and E. R. Shchukin (1976). *J. of Colloid and Int. Sci.* **57**, 564.

FIGURE CAPTION

Figure 1. Thermal Conductivity vs. Density. Circles and triangles represent physical substances. X's represent the formula, $k = 1.5 \times 10^{-13} D^{4.5} + .000155D + .024$. The symbols, \parallel and \perp , indicate heat conductivity measured parallel and perpendicular to the grain.

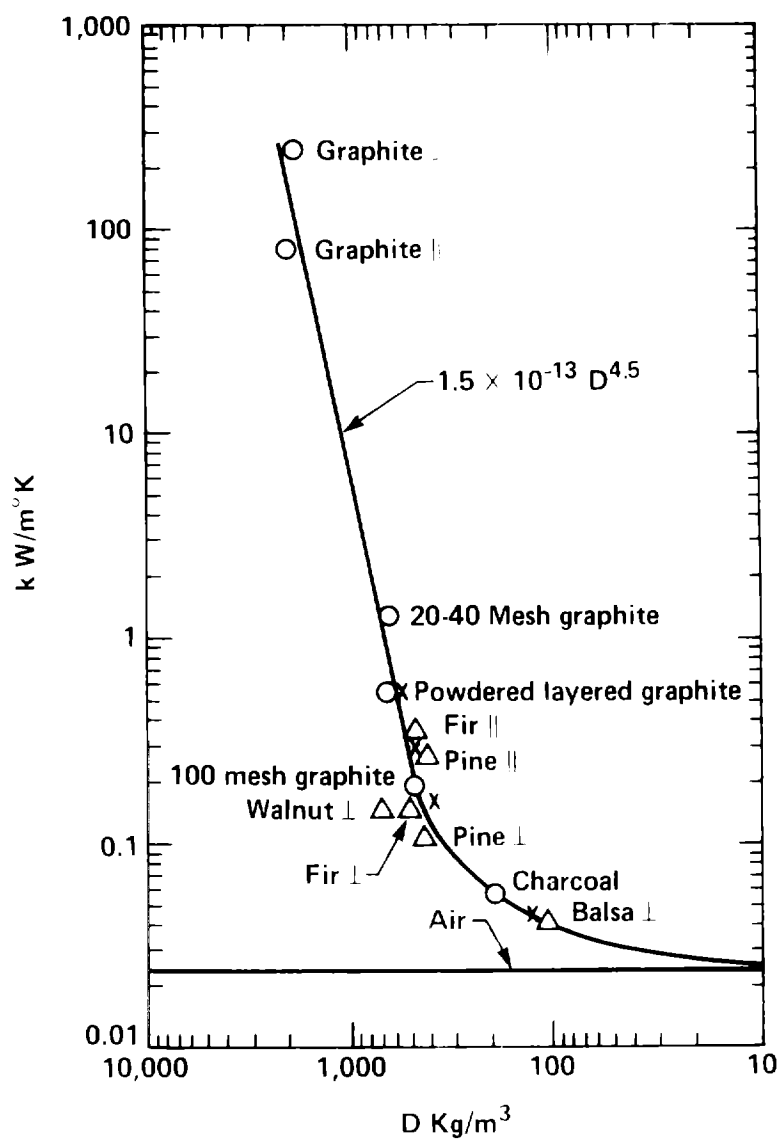


Figure 1.